

DIESTER PLASTICIZERS FROM MIXED CRAMBE DIBASIC ACIDS

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Twelve diesters prepared from a mixture of dibasic acids and individual alcohols having from four to 10 carbon atoms were evaluated as plasticizers for poly(vinyl chloride). The mixed dibasic acids, predominantly brassylic and azelaic, were obtained by ozonolysis of unsaturated fatty acids from crambe, a high-erucic acid oilseed. Monobasic acids produced by ozonolysis were easily removed by distillation. Use of the mixture of dibasic acids to make the "azela-brassylate" plasticizers requires neither isolation of individual fatty acids before ozonolysis nor separation of dibasic acids afterwards. All the azela-brassylates with six or fewer carbon atoms in the alcohol moiety were compatible; all compatible plasticizers, except for the dicyclohexyl ester, contributed excellent low-temperature flexibility to poly(vinyl chloride). Bis(2-methylpentyl) azela-brassylate had much better light stability than the bis(2-ethylhexyl) sebacate control and compared favorably in all other properties with this commercial, low-temperature plasticizer.

SELECTED diesters of brassylic (tridecanedioic) acid are excellent low-temperature plasticizers for poly(vinyl chloride) (PVC) (Nieschlag *et al.*, 1964). Subsequently, it was demonstrated that a combination of the best features of two different esters could be achieved in mixed products from simultaneous esterification of brassylic acid with the two appropriate alcohols (Nieschlag *et al.*, 1967a). Here we describe an alternative type of mixed-ester plasticizers, those in which a mixture of dibasic acids is esterified with a single alcohol.

Brassylic acid is produced by ozonolysis of erucic (*cis*-13-docosenoic) acid (Nieschlag *et al.*, 1967b). In turn, erucic acid comes from imported rapeseed oil or, more abundantly, from crambe oil now domestically available (*Chemical Engineering News*, 1966; U.S. Department of Agriculture, 1962; White and Wolff, 1966, 1967).

These oils also contain oleic, linoleic, and linolenic acids, all of which yield azelaic acid as one of their oxidative ozonolysis products. Therefore, if the total mixture of unsaturated fatty acids from saponification of a high-erucic seed oil is ozonized and then oxidized, the principal cleavage products are the dibasic acids, brassylic and azelaic, along with pelargonic (nonanoic) and other shorter chain monobasic acids. Removal of monobasic acids by distillation leaves the mixed dibasic acids that are esterified to yield diester plasticizers, herein after called "azela-brassylates."

Materials

The mixed dibasic acids were prepared in the laboratory by oxidative ozonolysis of crambe free fatty acids in a manner similar to that used to make brassylic acid from erucic acid (Nieschlag *et al.*, 1967b). Most of the saturated monobasic acids (mainly pelargonic) resulting from ozone cleavage of the unsaturated fatty acids were removed by vacuum distillation. Larger quantities of the mixture used to synthesize the diesters reported here were furnished by Emery Industries, Inc.

The product contained 93.3% dibasic acids as determined by gas-liquid chromatography (GLC) (Miwa *et al.*, 1960). The dibasic acids were predominantly brassylic (46.6%) and azelaic (31.3%) with lesser amounts of pentadecanedioic (2.2%), tetradecanedioic (0.3%), dodecanedioic (1.7%), undecanedioic (3.4%), sebacic (1.1%), suberic (2.8%), pimelic (1.7%), adipic (1.1%), and glutaric (0.9%). The rest of the product consisted of 4.5% of saturated, even-numbered, monobasic fatty acids derived unchanged from the original crambe acids and 2.2% of pelargonic acid not removed by vacuum distillation.

The alcohols were purchased from commercial sources as follows: 1-nonanol from Aldrich Chemicals; white label grade 2-methyl-1-propanol, 1-hexanol, 2-octanol, and 1-decanol from Eastman Organic Chemicals; reagent grade cyclohexanol from Fisher Scientific Co.; reagent grade 1-butanol and 1-octanol, chromatography 1-pentanol and 2-methyl-1-butanol from Matheson Scientific, Inc.; 2-methylpentanol and 2-ethylhexanol from Union Carbide Chemicals Co.

Preparation of Azela-Brassylate Diesters

Esterifications were conducted in a 500-ml., single-necked flask fitted with a Dean-Stark distilling trap and a condenser. A 20 mole % excess of alcohol was made to react with 50 grams of mixed dibasic acids in 190 ml. of benzene with 2.0 grams of *p*-toluenesulfonic acid as catalyst. The benzene removed water azeotropically from the reaction. The mixture was refluxed until no more water collected in the trap, which required 8 hours or less.

To remove the catalyst, the reaction mixture was washed several times with distilled water, twice with 5% sodium bicarbonate, and finally with distilled water until neutral. Almost all the benzene and some of the excess alcohol were removed *in vacuo* on a rotary evaporator.

The crude products contained some unreacted acid that was removed by passing the diester, dissolved in petroleum ether (b.p. 63° to 70° C.), through a column (1.5-cm. i.d.) containing

Table I. Analyses of Azela-Brassylate Diesters

Diester	Composition, % ^a			Sapon. Equiv. ^b		Acid Value ^c
	Pelargonate	Azelate	Brassylate	Calcd. ^d	Found	
<i>n</i> -Butyl	1.4	35.1	51.6	167	158	0.08
Isobutyl	1.3	31.0	47.4	167	160	0.17
<i>n</i> -Pentyl	1.0	36.8	46.3	180	183	0.06
Isopentyl	0.8	33.7	47.0	180	177	0.09
2-Methylpentyl	0.4	33.4	52.3	195	187	0.11
<i>n</i> -Hexyl	1.0	30.7	39.0	194	192	0.07
Cyclohexyl	0.7	33.3	41.0	191	192	0.05
2-Ethylhexyl	0.9	33.3	43.6	222	228	0.11
<i>n</i> -Octyl	0.7	29.6	44.5	221	186	0.31
2-Octyl	0.4	30.0	44.5	223	218	0.14
<i>n</i> -Nonyl	1.6	30.0	45.7	237	220	0.23
<i>n</i> -Decyl	0.0	32.1	45.6	251	259	0.27

^a Determined by gas-liquid chromatography; components not listed were esters of acids present in small amounts (see Materials). See Results and Discussion regarding variation in composition. ^b Method of VanEtten, 1951. ^c Sallee, 1962. ^d Calculated from gas-liquid chromatographic data.

30 grams of 80- to 200-mesh activated alumina (Matheson, Coleman and Bell No. 9296). After the column had been washed with petroleum ether, the diesters were recovered from the combined eluates by removal of solvent.

Final purification was accomplished by distillation at 5 microns of Hg in a molecular still. By this procedure the low-boiling contaminants (residual alcohol and some pelargonate ester) were removed as a forerun, and a substantial amount of colored material was left in the residue. The purified diesters had a slight yellowish color.

After purification, the diesters were analyzed for free acidity and free hydroxyl. Free hydroxyl was qualitatively determined by comparison of the infrared spectra (neat, liquid film) in the 3500- to 3600-cm.⁻¹ region with those of known standards.

Compositional data for the diesters given in Table I were obtained by temperature-programmed GLC with a 1/8 inch X 2 foot stainless steel column containing 3% JXR on 100/120-mesh Gas Chrom Q, a He flow of 2.5 ml. per minute, and a flame ionization detector. Temperature ranges (80° to 300° C.) and program rates (2° to 4° C. per minute) were tailored to give the best separation of components for each individual dialkyl azela-brassylate. The percentages of the two major components, brassylate and azelate, were used to calculate a theoretical saponification equivalent.

Evaluation of Azela-Brassylates as Plasticizers for PVC

Formulation. The azela-brassylates and two commercial plasticizers used for comparison were incorporated into a commercial PVC resin according to the following formulation:

	Parts by Weight
PVC (Geon 101)	65
Epoxidized oil (G-62)	1
Ba-Cd complex (Mark M)	2
Plasticizer	32

The plasticizer was added to the dry mixture of stabilizers and resin before milling. Milling was carried out on a 4 X 8 inch rubber mill at 160° C. for approximately 8 minutes. The plasticized sheet was then molded in a standard 6 X 6 X 0.075 inch mold. The mold containing the test formulation was first heated to 160° C. for 10 minutes without pressure, then pressed at 1000 p.s.i. for an additional 10 minutes at 160° C., and cooled under pressure to approximately room temperature. The molded sheets were equilibrated at 73° F. and 50% relative humidity for at least 24 hours before testing.

Compatibility. Observations made on the azela-brassylate-PVC compositions during and after milling and after molding gave the first indication of compatibility characteristics. The absence of surface exudate on molded sheets after storage in a laboratory room for 9 months was taken as evidence of excellent compatibility.

Physical Testing. Tensile properties, torsional stiffness temperatures, and losses due to migration and volatility were determined as reported earlier (Nieschlag *et al.*, 1964).

Heat and Light Stability. Heat stability was tested at 160° C. in an air-convection oven as previously described (Nieschlag *et al.*, 1964). The sample was considered to have failed when darkening reduced its transmittance to 20% at 600 mμ. Heat deterioration causes the azela-brassylate plasticized sheets to turn dark red or black.

Light stability of the azela-brassylates was determined with an Atlas Xenon Arc Fadeometer rather than the carbon arc used previously for the brassylate esters. During exposure to light from the xenon arc, specimens were subjected to a temperature of 80° C. with an air temperature of 60° C. at 5% relative humidity. Riser and Palm (1967b) found that the xenon and carbon arcs give comparable data. General failure due to exudation and stiffening is the same for either light source, although the xenon arc requires a slightly longer time for discoloration to develop.

Results and Discussion

The variation in relative amounts of brassylate and azelate shown for the diesters in Table I is probably due mainly to changes in composition during molecular distillation. Differences in GLC response could also account for some variation. However, the good agreement in most cases between calculated saponification equivalents and experimental values suggests that the GLC data are essentially correct. Analysis by GLC also confirmed infrared determinations, which indicated that only traces (<0.5% by weight) of free hydroxyl remained in the samples.

Properties of the azela-brassylates were compared with those of the corresponding dialkyl brassylates reported earlier (Nieschlag *et al.*, 1964).

Compatibility of the azela-brassylates, as determined by observations made during preparation and storage of the plasticized sheets, is presented in Table II. Mixed diesters with six carbon atoms, or less, in the alcohol moiety showed excellent compatibility with the resin. Esters made from eight or nine carbon alcohols were much less compatible; primary alcohol moieties appear to confer somewhat better compatibility than secondary alcohols. The didecyl ester was completely incompatible and could not be properly milled into PVC.

In comparison with the brassylate esters, the azela-brassylates showed somewhat improved compatibility; they remained compatible with the resin when esterified with alcohols of higher molecular weight—for example, the compatibility of dioctyl brassylate was similar to that of the dinonyl azela-

brassylate. Also, the 2-ethylhexyl derivative of the mixed acids had somewhat better compatibility than the corresponding brassylate.

Compatibility can also be evaluated from torsional data, as first pointed out by Riser and Palm (1967a). They suggest that the difference between $T_{135,000}$ and $T_{10,000}$ (which they call the compatibility number, ΔT) gives a qualitative indication of compatibility; low values indicate good compatibility (Table III).

A method of measuring stiffness in torsion as a function of temperature was introduced in 1942 by Clash and Berg, who arbitrarily selected an apparent modulus of elasticity of 135,000 p.s.i., $T_{135,000}$ (or T_f) temperature, as defining the borderline between a rigid and nonrigid material. As expected, we find

Table II. Compatibility of Azela-Brassylate Diesters with PVC

Diester Plasticizer	Observations	Compatibility
<i>n</i> -Butyl	Colorless, transparent. No exudate after 9 months	Excellent
Isobutyl	Colorless, transparent. No exudate after 9 months	Excellent
<i>n</i> -Pentyl	Colorless, transparent. No exudate after 9 months	Excellent
Isopentyl	Colorless, transparent. No exudate after 9 months	Excellent
2-Methylpentyl	Colorless, transparent. No exudate after 9 months	Excellent
<i>n</i> -Hexyl	Colorless, transparent. No exudate after 9 months	Excellent
Cyclohexyl	Colorless, transparent. No exudate after 9 months	Excellent
2-Ethylhexyl	Slight, greasy exudate after 5 days. Not greatly increased after 9 months	Fair to good
<i>n</i> -Octyl	Light greasy exudate 24 hours after molding. Cloudy, transparent	Fair
2-Octyl	Cloudy, translucent. Heavy exudate on cooling to room temperature	Very poor
<i>n</i> -Nonyl	Cloudy, translucent. Exudate on cooling to room temperature. Heavy dry white exudate after 24 hours	Very poor
<i>n</i> -Decyl	Did not fuse properly	None

that the $T_{135,000}$ point usually lies near the upper inflection of the sigmoidal torsional modulus *vs.* temperature curves. The temperature at which a stiffness of 10,000 p.s.i. is observed, $T_{10,000}$ (or T_d), is significant because it usually falls in the most linear portion of the curve.

Compatibility can be even better evaluated if ΔT is plotted *vs.* the $T_{135,000}$ temperature as in Figure 1. The straight line was plotted from data for three widely used, commercial plasticizers: tricresyl phosphate (TCP), bis(2-ethylhexyl) phthalate (DOP), and bis(2-ethylhexyl) azelate (DOZ). Since the plot has been expanded to show data for the test plasticizers in

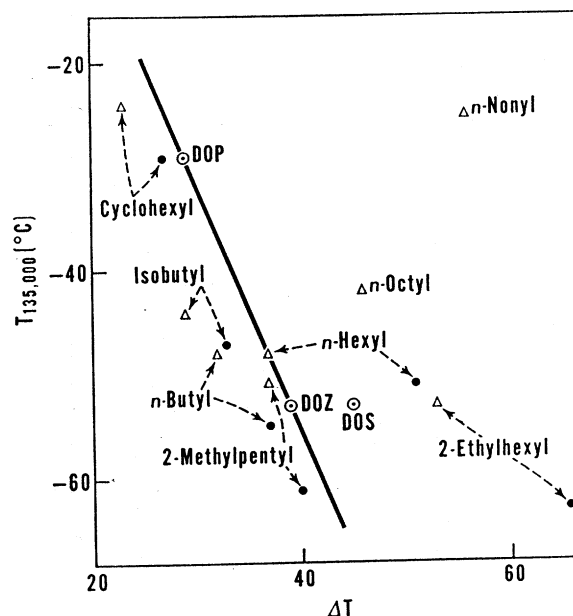


Figure 1. Compatibility from torsional data of dialkyl azela-brassylates (Δ) *vs.* dialkyl brassylates (\bullet) and standards (\odot)

Alkyl groups are as named: DOS = bis(2-ethylhexyl) sebacate; $\Delta T = [T_{135,000} (^{\circ}\text{C}) - T_{10,000} (^{\circ}\text{C})]$. The reference line was drawn from data for tricresyl phosphate ($T_{135,000} = -2^{\circ}\text{C}$; $\Delta T = 18^{\circ}\text{C}$), bis(2-ethylhexyl) phthalate (DOP), and bis(2-ethylhexyl) azelate (DOZ) (Riser and Palm, 1967a). Plasticizers on the left of this line are considered more compatible than the graphical standards and those to the right less.

Table III. Properties of Molded PVC Sheets Containing Azela-Brassylate Diesters

Diester Plasticizer	Tensile Properties			Torsional Stiffness Temperature, $^{\circ}\text{C}$.		Compatibility Number, ^a ΔT	Migration, Wt. Loss, %	Volatility, Wt. Loss, %
	Tensile, p.s.i.	100% modulus, p.s.i.	Elongation, %	$T_{135,000}$	$T_{10,000}$			
<i>n</i> -Butyl	2560	760	350	-48	-16	32	20.7	8.9
Isobutyl	2600	830	350	-44	-15	29	16.6	10.6
<i>n</i> -Pentyl	2590	850	370	-49	-15	34	21.4	5.3
Isopentyl	2715	990	320	-48	-13	35	19.1	6.9
2-Methylpentyl	2590	940	300	-51	-14	37	19.2	3.7
<i>n</i> -Hexyl	2600	920	330	-48	-11	37	20.9	2.9
Cyclohexyl	2840	1095	300	-24	-1	23	5.1	1.7
2-Ethylhexyl	2620	1095	300	-53	0	53	19.3	2.4
<i>n</i> -Octyl	2290	940	315	-42	4	46	26.2 ^b	5.8 ^b
2-Octyl	2570	1350	300	-51	32	83	19.9 ^b	11.9 ^b
<i>n</i> -Nonyl	2470	1240	280	-25	32	57	^c	^c
Incompatible								
Controls								
Bis(2-ethylhexyl) phthalate (DOP)	2890	1260	270	-26	0	26	4.3	1.6
Bis(2-ethylhexyl) sebacate (DOS)	2610	990	380	-53	-8	45	19.6	1.3

^a Riser and Palm, 1967a. ^b Data are questionable because heavy exudate was present before test. ^c Not tested because of excessive white, crystalline exudate.

greater detail, the point representing TCP ($T_{135,000} = -2^\circ \text{C.}$, $\Delta T = 18$) is off scale and not shown. After study of a number of plasticizers, Riser and Palm (1967a) showed that the proximity of the $T_{135,000}$ vs. ΔT point to such a reference line gives an indication of the compatibility of a plasticizer in PVC. The farther to the right of this line the point falls, the poorer the expected compatibility. Data points that fall on the line or to the left of it suggest that the plasticizer represented will have good compatibility with the resin. In Figure 1, data for comparable brassylates and azela-brassylates are included on the same plot. Because the points for most of the azela-brassylates are farther to the left than points for the brassylates, the mixed diesters apparently are the more compatible plasticizers.

Tensile properties (Table III) of the azela-brassylates are essentially the same as those of the corresponding brassylates. The relatively low modulus values for the compatible azela-brassylates show that they are efficient plasticizers comparable to bis(2-ethylhexyl) sebacate (DOS) and somewhat better than DOP.

Except for the dicyclohexyl ester, all compatible azela-brassylates have excellent low-temperature flexibility. The flex temperatures ($T_{135,000}$ or T_f) of these diesters are only 3° to 10°C. higher than those reported previously for brassylate esters of the same chain length. The 2-methylpentyl ester has the lowest flex temperature (-51°C.) of the compatible azela-brassylates and is almost equal to the DOS control (-53°C.). All the compatible straight-chain esters have lower $T_{10,000}$ temperatures than the commercial control plasticizers. Comparison of the $T_{135,000}$ and $T_{10,000}$ temperatures shows a relatively gradual increase in stiffness as temperature is lowered. This desirable characteristic was also noted with the brassylate diesters.

Migration losses of the azela-brassylates are slightly improved over the corresponding brassylate esters. In general, the compatible, noncyclic esters have migration losses comparable to the DOS control. Losses due to volatility tend to decrease as chain length increases. The azela-brassylates have somewhat higher volatility than the corresponding brassylates.

Like the brassylates, most of the azela-brassylates have good heat stability at 160°C. (Table IV). The loss on heating roughly parallels the volatility loss, with the longer chain esters tending to lose less weight.

Table IV. Heat and Light Stability of Molded PVC Sheets Containing Azela-Brassylate Diesters

Diester Plasticizer	Heat Stability at 160°C.		Light Stability (Xenon Arc)	
	Hours to failure	Wt. loss at failure, %	Hours	Failure
n-Butyl	6.2	21.3	840	Stiffening
Isobutyl	5.4	19.4	720	Stiffening
n-Pentyl	5.9	15.3	840	Exudate
Isopentyl	5.6	16.7	840	Exudate
2-Methylpentyl	5.4	13.0	456	Exudate
n-Hexyl	6.3	12.7	288	Exudate
Cyclohexyl	6.7	7.7	1010	Exudate
2-Ethylhexyl	6.6	5.9	48	Exudate
n-Octyl	6.0	4.2	0	Exudate
2-Octyl	6.0	7.2	0	Exudate
n-Nonyl	6.0	2.5	0	Exudate
n-Decyl	Incompatible			
Controls				
Bis(2-ethylhexyl) phthalate (DOP)	6.4	10.0	1010	Exudate and stiffening
Bis(2-ethylhexyl) sebacate (DOS)	6.7	6.1	240	Exudate

Light stability of the azela-brassylates is comparable to, or possibly slightly better than, the brassylates. All the compatible azela-brassylates had better light stability than the DOS control.

The 2-methylpentyl ester appears to be the best of the azela-brassylates and compares favorably with DOS as a low-temperature plasticizer. Although bis(2-methylpentyl) azela-brassylate has slightly more volatility with somewhat less heat stability than DOS, it has a slightly lower migration loss and much better light stability than the commercial control.

Comparison of DOP and dicyclohexyl azela-brassylate shows these two plasticizers to be remarkably similar in almost all respects. This similarity with DOP was also noted with the dicyclohexyl brassylate. These plasticizers exhibit outstanding light stability with very low migration and volatility losses. Figure 1 suggests that the dicyclohexyl-brassylate and azela-brassylate are somewhat more compatible with PVC than DOP.

Conclusions

Plasticized PVC sheets containing 32% of compatible "azela-brassylate" diesters, except for the dicyclohexyl ester, exhibit excellent low-temperature flexibility. Sheets containing dicyclohexyl azela-brassylate have properties almost identical to those of sheets containing DOP; both plasticizers have low migration and volatility losses with excellent heat and light stabilities.

The bis(2-methylpentyl) azela-brassylate ester compares favorably with commercial DOS as a low-temperature plasticizer for PVC; in addition, the mixed ester has much better light stability.

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